

# PATENT SPECIFICATION

(11) 1 480 704

1 480 704

(21) Application No. 8135/75 (22) Filed 26 Feb. 1975  
 (31) Convention Application No. 49/022526 (32) Filed 26 Feb. 1974 in  
 (33) Japan (JA)  
 (44) Complete Specification published 20 July 1977  
 (51) INT CL<sup>2</sup> G03C 1/06  
 (52) Index at acceptance  
 G2C C19E2A C19J3G C19JY C19K11



## (54) THERMALLY DEVELOPABLE LIGHT-SENSITIVE PHOTOGRAPHIC MATERIAL

(71) We, FUJI PHOTO FILM CO., LTD., a Japanese Company, of No. 210, Nakanuma, Minami-Ashigara-Shi, Kanagawa, Japan, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a thermally developable light-sensitive photographic material, capable of providing a contrasty image and thus able to be subjected to reflection printing, and a method of making such a material.

Thermally developable light-sensitive photographic materials are described in U.S. Patents Nos. 3,152,904, 3,457,075, 3,635,719, 3,645,739, 3,756,829, 3,589,903, 3,802,888, 3,764,329, 3,672,904, 3,846,136, 3,839,041, 3,708,304, 3,761,279, 3,751,249, 3,770,448 and 3,773,512, Canadian Patent 811,677, and Japanese Patent Application (OPI) Nos. 4728/1971 and 89720/1973, and these comprise a light-sensitive layer containing, as a principal component, a silver salt of a long chain aliphatic carboxylic acid such as silver behenate, silver saccharin or silver benzotriazole, and a catalytic amount of light-sensitive silver halide.

In these thermally developable light-sensitive photographic materials, however, a high contrast image with satisfactory quality cannot be obtained and these material are unsatisfactory when a high

suitable for reflection printing would therefore be desirable.

In accordance with the invention, there is provided a thermally developable light-sensitive photographic material comprising a support having thereon in at least one layer

- (a) an organic silver salt,
- (b) a catalytic amount of a light-sensitive silver halide, or a halogen compound capable of reacting with the organic silver salt (a) to form a catalytic amount of light-sensitive silver halide,
- (c) a reducing agent capable of reducing said organic silver salt to silver in the presence of an imagewise exposed catalytic amount of light-sensitive silver halide, and
- (d) a rhodium compound selected from rhodium nitrate and



wherein M represents a monovalent cation, X represents a halogen atom, h is from 2 to 5, k is 1 or 2, l is from 5 to 11, m is 0 or 2, and p is from 0 to 12, said rhodium compound being in contact with the components (a) and (b).

The organic silver salt (a) should be reasonably stable towards light and be colourless, white or but slightly coloured, and should form silver (to form images) upon being heated above 80°C.

50

55

60

65

70

75

## ERRATA

### SPECIFICATION No. 1,480,704

Page 2, line 21, for mercapton read mercapto  
 Page 2, line 21, delete of insert or  
 Page 3, line 127, for accordance read  
 accordance  
 Page 4, line 7, for silvert read silver  
 Page 6, line 77, for 1873 read 1973  
 Page 12, line 47, delete hale insert halide

THE PATENT OFFICE  
 19th September, 1977

35 n  
 us  
 th  
 tai  
 is  
 40 Sy.  
 Inc  
 ( abl  
 met  
 45 Fuj  
 vidt  
 be  
 all  
 matu

# PATENT SPECIFICATION

(11) 1 480 704

1 480 704

(21) Application No. 8135/75 (22) Filed 26 Feb. 1975  
 (31) Convention Application N. 49/022526 (32) Filed 26 Feb. 1974 in (19)  
 (33) Japan (JA)  
 (44) Complete Specification published 20 July 1977  
 (51) INT CL<sup>2</sup> G03C 1/06  
 (52) Index at acceptance

G2C C19E2A C19J3G C19JY C19K11



(54) THERMALLY DEVELOPABLE LIGHT-SENSITIVE  
 PHOTOGRAPHIC MATERIAL

(71) We, FUJI PHOTO FILM CO., LTD., a Japanese Company, of No. 210, Nakanuma, Minami-Ashigara-Shi, Kanagawa, Japan, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a thermally developable light-sensitive photographic material, capable of providing a contrasty image and thus able to be subjected to reflection printing, and a method of making such a material.

Thermally developable light-sensitive photographic materials are described in U.S. Patents Nos. 3,152,904, 3,457,075, 3,635,719, 3,645,739, 3,756,829, 3,589,903, 3,802,888, 3,764,329, 3,672,904, 3,846,136, 3,839,041, 3,708,304, 3,761,279, 3,751,249, 3,770,448 and 3,773,512, Canadian Patent 811,677, and Japanese Patent Application (OPI) Nos. 4728/1971 and 89720/1973, and these comprise a light-sensitive layer containing, as a principal component, a silver salt of a long chain aliphatic carboxylic acid such as silver behenate, silver saccharin or silver benzotriazole, and a catalytic amount of light-sensitive silver halide.

In these thermally developable light-sensitive photographic materials, however, a high contrast image with satisfactory quality cannot be obtained and these material are unsatisfactory when a high contrast sensitive material is required, for example, when a negative is obtained from a positive original using a reflection printing method and, using this negative as an original, a positive is obtained again. The reflection printing method is described in J. Kosar: *Light-Sensitive Systems*, page 290—291, John Wiley & Sons, Inc., New York (1965).

One silver halide sensitised material suitable for an analogous reflection printing method is Quick Copy Paper manufactured by Fuji Photo Film Co., Ltd. This material provides an excellent image quality but must be processed with liquid compositions, with all their attendant disadvantages. Sensitised materials processable in the dry state and

suitable for reflection printing would therefore be desirable. 50

In accordance with the invention, there is provided a thermally developable light-sensitive photographic material comprising a support having thereon in at least one layer

(a) an organic silver salt,  
 (b) a catalytic amount of a light-sensitive silver halide, or a halogen compound capable of reacting with the organic silver salt (a) to form a catalytic amount of light-sensitive silver halide,  
 (c) a reducing agent capable of reducing said organic silver salt to silver in the presence of an imagewise exposed catalytic amount of light-sensitive silver halide, and  
 (d) a rhodium compound selected from rhodium nitrate and



wherein M represents a monovalent cation, X represents a halogen atom, *b* is from 2 to 5, *k* is 1 or 2, *l* is from 5 to 11, *m* is 0 or 2, and *p* is from 0 to 12, said rhodium compound being in contact with the components (a) and (b).

The organic silver salt (a) should be reasonably stable towards light and be colourless, white or but slightly coloured, and should form silver (to form images) upon being heated above 80°C, preferably above 100°C, by reaction with a reducing agent but only in the presence of a catalytic amount of exposed silver halide. Suitable examples of organic silver salts (a) include the silver salts of organic compounds having an imino group, a mercapto group, a thio group, a hydroxy group, or a carboxyl group, especially the silver salts of fatty acids. Suitable specific examples of these compounds are given in the following List 1.

List 1

(1) Silver salts of compounds having an imino group, silver salt or benzotriazole, silver salt of nitrobenzotriazole, silver salt of an alkyl-substituted benzotriazole (e.g. silver salt of methyl-

55

60

65

70

75

80

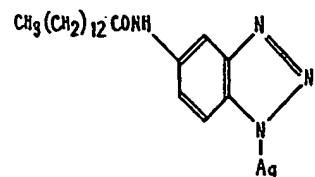
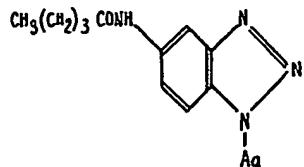
85

90

95

5 benzotriazole), silver salt of a halogen-substituted benzotriazole (e.g. silver salt of bromobenzotriazole and silver salt of chlorobenzotriazole), silver salt of a carboimido-substituted benzotriazole (e.g.

or



10 silver salt of a substituted benzimidazole (e.g. silver salt of 5 - chloro - benzimidazole or silver salt of 5-nitrobenzimidazole), silver salt of carbazole, silver salt of saccharin, silver salt of phthalazinone, silver salt of a substituted phthalazinone, silver salt of a phthalimide, silver salt of a pyrrolidone, silver salt of tetrazole and silver salt of imidazole;

15 (2) Silver salts of compounds having a mercapton group of a thio group: silver salt of 3 - mercapto - 4 - phenyl - 1,2,4 - triazole, silver salt of 2 - mercapto - benzimidazole, silver salt of 2 - mercapto - 5 - aminothiadazole, silver

20 salt of 1 - phenyl - 5 - mercaptotetrazole, silver salt of 2 - mercaptobenzothiazole, silver salt of 2 - (S - ethylthioglycolamido) - benzothiazole, silver thioglycolates as described in Japanese Patent Application (OPI) No. 2822/73 (e.g. silver S-alkyl (C<sub>12</sub>-C<sub>22</sub>) thioglycolate), silver dithiocarboxylate (e.g. silver dithioacetate), silver salt of thioamide, silver salt of thiopyridine (e.g. silver salt of 5 - carbethoxy - 1 - methyl - 2 - phenyl - 4 - thiopyridine), silver salt of dithiodihydroxybenzole, silver salt of mercaptotriazine, silver salt of 2 - mercaptobenzoxazole and silver salt of mercaptooxadiazole;

25 (3) Silver salts of compounds having a carboxy group: (i) silver salts of aliphatic carboxylic acids; silver caprate, silver laurate, silver myristate, silver palmitate, silver stearate, silver behenate, silver maleate, silver fumarate, silver tartrate, silver furoate, silver linoleate, silver oleate, silver hydroxystearate, silver adipate, silver sebacate, silver succinate, silver acetate, silver

30 butyrate and silver camphorate; (ii) silver salts of aromatic carboxylic acids and thers: silver benzoate, substituted silver benzoate (e.g. silver 3,5 - dihydroxybenzoate, silver o - methyl - benzoate, silver m - methylbenzoate, silver p - methylbenzoate, silver 2,4 - dichlorobenzoate, silver acetamido-benzoate and silver p - phenylbenzoate), silver gallate, silver tannate, silver phthalate, silver terephthalate, silver salicylate, silver phenylacetate, silver pyromellitate, silver salt of 4' - n - octadecyloxydiphenyl - 4 - carboxylic acid, silver salt of a thion-carboxylic acid as described in U.S. Patent 3,785,830 and silver salt of an aliphatic carboxylic acid having a thio-ether group as described in U.S. Patent 3,330,663;

35 (4) Other silver salts: silver salt of 4 - hydroxy - 6 - methyl - 1,3,3a,7 - tetraazaindene, silver salt of 5 - methyl - 7 - hydroxy - 1,2,3,4,6 - pentaazaindene, silver salt of tetraazaindene as described in British Patent 1,230,642, silver salt of S - 2 - aminophenylthio-sulphuric acid as described in U.S. Patent 3,549,379, silver salt of a metal-containing aminoalcohol as described in Japanese Patent Application (OPI) No. 6586/71 and silver salt of an organic acid metal chelate as described in Belgian Patent 768,411.

40 These organic silver salts are generally prepared by mixing a solution of a silver-salt-forming organic compound (e.g. benzotriazole dissolved in methanol) with an aqueous solution of a silver salt such as silver nitrate or a silver complex salt. A suitable method is described in Japanese Patent Publication 30270/1969 and comprises mixing a solution of silver nitrate dissolved in a solvent A with a solution of benzotriazole dissolved in a solvent B. Solvent A dissolves silver nitrate and nitric acid easily but silver benzotriazole only slightly, and may be water, dimethylformamide or dimethyl sulphoxide. Solvent B dissolves benzotriazole easily but not (or only slightly) silver benzotriazole and silver nitrate. Solvent B has a solubility in solvent A of 1 to 30% by weight based on the total solvents A+B, and may be a phosphoric acid ester, a phthalic acid ester or a dibasic fatty acid ester of an alcohol or phenol or a higher fatty acid ester of glycerin, such as tricresyl phosphate, dimethoxyethyl phthalate, di-n - butyl phthalate, diethyl sebacate, monoocetyl-dibutyl phosphate, tributyl phosphate, castor oil or linseed oil. Other organic silver salts can often be prepared by analogous methods.

45 A suitable method of preparing organic silver salts such as silver salts of organic carboxylic acids, such as silver laurate, silver caprate, silver myristate, silver palmitate,

55

60

65

70

75

80

85

90

95

100

105

110

115

silver stearate, silver behenate, silver adipate and silver sebacate, comprises mixing an aqueous solution of a water-soluble carboxylic acid salt, for example, an alkali metal salt such as the sodium, potassium or lithium salt or the ammonium salt, with an aqueous solution of silver nitrate.

Furthermore, a silver salt of an organic carboxylic acid can be prepared by mixing a first solution (of an organic carboxylic acid) with a second solution. The first solvent is capable of dissolving the organic carboxylic acids but only slightly of dissolving organic carboxylic acid silver salts and silver nitrate and is itself only slightly soluble in water, and may be phosphoric acid esters such as tricresyl phosphate, tributyl phosphate and monoxyethyl dibutyl phosphate, phthalic acid esters such as diethyl phthalate, dibutyl phthalate, dimethyl phthalate, diethyl phthalate and dimethoxy ethyl phthalate, carboxylic acid esters such as pentyl acetate, isopropyl acetate, isopentyl acetate, ethyl acetate, 2 - ethylbutyl acetate, butyl acetate, propyl acetate, diethyl sebacate, diethyl succinic acid, ethyl formate, propyl formate, butyl formate, pentyl formate, ethyl pentanoate, diethyl tartrate, methyl butanoate, ethyl butanoate, butyl butanoate and isopentyl butanoate, glycerin esters of higher fatty acids such as castor oil, aromatic hydrocarbons such as benzene, toluene and xylene, aliphatic hydrocarbons such as *n*-hexane and cyclohexane, if necessary emulsified with water or an alkaline aqueous solution such as an aqueous solution of sodium hydroxide, an aqueous solution of potassium hydroxide or an aqueous solution of ammonia. The second solution is an aqueous solution of silver nitrate or a silver complex salt, preferably, an alkali-soluble silver complex salt having a higher dissociation constant than the silver salt of the organic acid, for example, silver ammine complex salt, silver methylamine complex salt or silver ethylamine complex salt. Another method comprises mixing an emulsion of an aqueous solution of a salt of an organic carboxylic acid, for example, the sodium, potassium or ammonium salt and the above described solvent only slightly soluble in water with an aqueous solution of a silver salt such as silver nitrate or a silver complex salt. These methods can be adapted for the preparation of other organic silver salts as well.

These methods of preparing organic silver salts are described in, for example, U.S. Patent No. 3,458,544, Japanese Patent Publication No. 30270/1969, German OLS Nos. 2,322,096, 2,401,159 and 2,402,906, French Patent No. 2,147,286 and Japanese Patent Application No. 49436/1969.

Component (b) used in the invention can be prepared by the method of German OLS No. 2,428,125 in which the organic silver salt (a) is made in the presence of a silver-

halide-forming component and further in the presence of a rhodium compound (in accordance with this invention).

The silver-halide-forming component may be added to a solution of an organic carboxylic acid or its salt to form a solution, emulsion or dispersion. (For simplicity, the description will refer to the preparation of a silver carboxylate but is also generally applicable to the preparation of other organic silver salts). Alternatively the solution of an organic carboxylic acid or its salt and a solution of a silver salt such as silver nitrate or a silver complex salt are mixed with a solution, dispersion or emulsion of the silver-halide-forming component. In accordance with the invention a rhodium compound may be present in any of the above-described solutions, dispersions or emulsions or may be added in the form of a previously prepared solution, dispersion or emulsion.

According to the above-described method, the rhodium compound is caused to be present simultaneously with or before the addition of the silver-halide-forming component. It is also possible to form a material according to the invention by making the silver salt (a) in the presence of a silver-halide-forming component, and adding the rhodium compound (d) subsequently, but in this case the effect of the rhodium compound is less.

Another more preferred method of forming a catalytic light-sensitive silver halide (b) comprises reacting a silver-halide-forming component with a previously prepared stoichiometric excess of an organic silver salt (a) thus converting a part of the organic silver salt into silver halide, as generally described in U.S. Patent No. 3,457,075 and British Patent Application No. 48518/74. In this method, a rhodium compound is present in a dispersion of the organic silver salt (a) or in a solution or dispersion of the silver-halide-forming component or in its solution or dispersion before or after the silver-halide-forming component is added to the reaction vessel. The sensitivity and other characteristics can be improved by ripening at a high temperature, for example 30° to 80°C, for a suitable time such as 20 minutes to 3 hours, after the addition to the reaction vessel of the rhodium compound and/or the silver-halide-forming component.

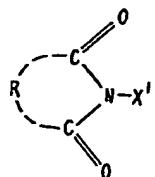
A further method of forming a material according to the invention comprises mixing a previously prepared catalytic amount of silver halide (b) with an organic silver salt (a), as described in British Patents Nos. 1,362,970, 1,354,186 and 1,469,116, French Patent No. 2,078,586 and U.S. Patents Nos. 3,152,904, 3,706,564, 3,706,565 and 3,713,833, but modified in accordance with this invention by the presence of the rhodium compound (d) when the organic silver salt (a) and the silver halide (b) are mixed. Again,

it is possible to form a material according to the invention by adding the rhodium compound (d) after mixing the organic silver salt and the silver salt, in which case the effect of the rhodium compound is less.

Any compound capable of forming a silver halide by reaction with an organic silver salt can be used as a silver-halide-forming component. Routine tests can be easily performed to determine which silver-halide-forming component is more effective, and consist in reacting a silver-halide-forming component with an organic silver salt and then examining the X-ray diffraction characteristics of the products including any silver halide formed.

Examples of suitable silver-halide-forming components are the chlorides, bromides or iodides of hydrogen, ammonium or a metal such as lithium, sodium, potassium, rubidium, caesium, copper, gold, beryllium, magnesium, calcium, strontium, barium, zinc, cadmium, mercury, aluminium, gallium, indium, thallium, germanium, tin, lead, antimony, bismuth, chromium, molybdenum, tungsten, manganese, rhenium, ruthenium, palladium, osmium, rhodium, iridium or platinum.

Other examples of silver-halide-forming components are halogen-containing metal complexes such as  $K_2PtCl_6$ ,  $K_2PtBr_6$ ,  $HAuCl_4$ ,  $(NH_4)_2IrCl_6$ ,  $(NH_4)_2RuCl_6$  and  $(NH_4)_3(RuCl_6)$ . Preferred examples are N-halo compounds having a —CONX'— group wherein X' represents Cl, Br or I, such as N - haloacetamides, N - halophthalazinones and N - halosuccinimides

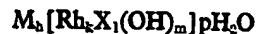


wherein R represents a group of atoms completing a 5- or 6-membered ring. Further examples of silver-halide-forming components are onium halides such as cetyl ethyldimethylammonium bromide and trimethylbenzylammonium bromide, halogenated hydrocarbons such as triiodomethane, tribromomethane, 2 - bromo - 2 - methylpropane and tetrabromomethane, and halogen - containing compounds such as triphenylmethyl chloride, triphenylmethyl bromide, 2 - bromobutanoic acid, 2 - bromoethanol and benzophenone dichloride.

The above-described silver-halide-forming components can be used individually or in combination. The quantity of the component used is generally from 0.001 to 0.5 mole, preferably 0.01 to 0.2 moles, per mole of the organic silver salt (a). If too little is used, the sensitivity is lessened, while if too much is used, gradual discolouration and a consequent decrease in contrast between the image

area and the background occur when the developed material is allowed to stand in the light.

The rhodium halides such as rhodium chloride and rhodium bromide given as examples of the silver-halide-forming component must not be confused with the rhodium compound in the presence of which, according to the present invention, the light-sensitive silver halide is formed. The rhodium complex has the formula

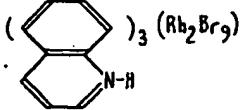
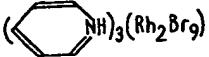
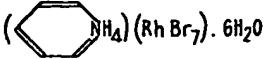
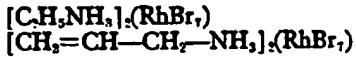
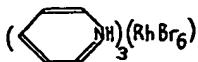


M represents a monovalent cation (preferably an alkali metal ion such as a lithium, sodium or potassium ion, or an onium ion such as a pyridinium ion, a dimethylammonium ion, a tetramethylammonium ion or a tetraethylammonium ion or an ammonium ion, a quaternary ammonium ion (e.g. tetramethylammonium and tetraethylammonium) being especially preferred). X represents any halogens, e.g. chlorine, bromine or iodine, preferably chlorine or bromine; that is, more than one halogen (e.g. chlorine and bromine) can be present in the same rhodium compound. h represents an integer or 2 to 5, k represents an integer of 1 or 2, l represents an integer of 5 to 11, m represents an integer of 0 or 2, and p represents an integer of 0 to 12.

Typical examples of rhodium compounds of the above general formula are given in the following List 2:

List 2

$K_2(RhCl_6)$	95
$K_2[RhCl_6(OH)_2]$	
$(NH_4)_2[RhCl_6(OH)_2]$	
$Na[RhCl_6(OH)_2]$	
$Rb_2[RhCl_6(OH)_2]$	
$Cs_2[RhCl_6(OH)_2]$	
$Li_2(RhCl_6) \cdot 12H_2O$	100
$Na_3(RhCl_6) \cdot 12H_2O$	
$Li_3(RhCl_6) \cdot 6H_2O$	
$Na_3(RhCl_6) \cdot 10H_2O$	
$Na_3(RhCl_6) \cdot 6H_2O$	
$Na_3(RhCl_6) \cdot 2H_2O$	
$Na_3(RhCl_6)$	105
$K_2(RhCl_6) \cdot H_2O$	
$(NH_4)_2(RhCl_6) \cdot 12H_2O$	
$(NH_4)_2(RhCl_6) \cdot H_2O$	
$[(CH_3)_2NH_2]_2(RhCl_6)$	110
$(CH_3NH_2)_2(RhCl_6)$	
$[(C_2H_5NH_2)_2(RhCl_6)]$	
$[(CH_3)_2N]_2(RhCl_6)$	
$[(CH_3CH_2)_2N]_2(RhCl_6)$	
$K_2(RhBr_6)$	
$(NH_4)_2(RhBr_6)$	115
$Rb_2(RhBr_6)$	
$Na_3(RhBr_6) \cdot 12H_2O$	
$Na_3(RhBr_6) \cdot H_2O$	
$Na_3(RhBr_6)$	



10     Rhodium nitrate is another rhodium compound which can be used in this connection. These compounds can be used individually or as a combination of two or more.

15     The rhodium compound is used generally in an amount of from 0.0001 to 0.5 moles, preferably 0.001 to 0.1 moles, per mole of the silver halide or silver-halide-forming component (b).

20     The reducing agent (c) may be any compound capable of reducing the organic silver salt (a) to produce a silver image when heated in the presence of exposed silver halide as a catalyst. Substituted phenols, substituted or unsubstituted bisphenols, substituted or unsubstituted mono- or bisnaphthols, di- or polyhydroxybenzenes, di- or polyhydroxynaphthalenes, hydroquinone monoethers, ascorbic acid or its derivatives, 3-pyrazolidones, pyrazoline - 5 - ones, reducing saccharides, *p* - phenylenediamine or its derivatives, amino-reductones, kojic acid and 4 - isopropyltropone can be used.

25     These reducing agents are described in U.S. Patents No. 3,152,904, 3,457,075, 3,531,286, 3,589,903, 3,756,829, 3,679,426, 3,667,958, 3,672,904, 3,751,249, 3,770,448, 3,773,512 and 3,819,382, Japanese Patent Application No. 27242/1973, German OLS 2,434,415, Belgian Patent No. 786,086 and Canadian Patent 811,677.

30     Examples of suitable reducing agents are given in the following List 3:

List 3

45     (1) substituted phenols:  
*p* - aminophenol, *o* - aminophenol,  
N - methyl - *p* - aminophenol, 2 -  
methoxy - 4 - aminophenol, 2,4 - di-  
aminophenol, 2 -  $\beta$  - hydroxyethyl -  
4 - aminophenol, *p* - *t* - butylphenol,

*p* - *t* - amylophenol, *p* - cresol, *p* -  
acetophenol, 2,6 - di - *t* - butyl - *p* -  
cresol, *p* - phenylphenol, *p* - ethyl-  
phenol, *p* - *sec* - butylphenol, *o* -  
phenylphenol, 1,4 - dimethoxyphenol,  
*p* - acetoacetyl - 4 - methylphenol,  
2,3 - dimethylphenol, 3,4 - xylenol,  
2,4 - xylenol, 2,6 - dimethoxy - 3,4,5 -  
trimethylphenol, 2,4 - di - *t* - butyl-  
phenol, phenol, 3,5 - di - *t* - butyl -  
4 - hydroxybenzylidimethylamine,  
chlorothymol,  $\alpha$  - phenyl - *o* - cresol,  
*p* - nonylphenol and *p* - octylphenol.

(2) Substituted or non-substituted bis-  
phenols:

bisphenol A, 1,1 - bis(2 - hydroxy -  
3,5 - dimethylphenyl) - 3,5,5 - tri-  
methylhexane, 2,4,4 - trimethylpentyl -  
bis(2 - hydroxy - 3,5 - dimethyl-  
phenyl)methane, bis(2 - hydroxy - 3 -  
*t* - butyl - 5 - methylphenyl)methane,  
bis(2 - hydroxy - 3,5 - di - butyl-  
phenyl)methane, 4,4' - methylene -  
bis(3 - methyl - 5 - *t* - butylphenol),  
4,4' - methylene - bis(2,6 - di - *t* -  
butylphenol), 2,2' - methylene - bis -  
(2 - *t* - butyl - 4 - ethylphenol), 2,6 -  
methylen - bis - (2 - hydroxy - 3 - *t* -  
butyl - 5 - methylphenyl) - 4 - methyl-  
phenol, 3,3',5,5' - tetra - *t* - butyl -  
4,4' - dihydroxybiphenyl, 1,1 - bis -  
(4 - hydroxyphenyl) - cyclohexane,  
1,1 - bis - (5 - chloro - 2 - hydroxy-  
phenyl)methane, 2,2 - bis(3,5 - di-  
bromo - 4 - hydroxyphenyl)propane,  
2,2 - bis - (4 - hydroxyphenyl) - pro-  
pane, 2,2 - bis(3,5 - dimethyl - 4 -  
hydroxyphenyl)propane, 2,2 - bis -  
(3 - methyl - 4 - hydroxyphenyl)pro-  
pane, bis(3 - methyl - 4 - hydroxy -  
5 - *t* - butylphenyl)sulphide,  $\alpha\alpha'$  -  
(3,5 - di - *t* - butyl - 4 - hydroxy-  
phenyl)dimethyl ether, N,N' - di(4 -  
hydroxyphenyl)urea, diethylstilbestrol  
and hexestrol.

(3) Substituted or non-substituted mono-  
or bisnaphthols and di- or polyhydroxy-  
naphthalenes:

sodium 1 - amino - 2 - naphthol - 6 -  
sulphonate, 1 - naphthylamine - 7 -  
sulphonic acid, 1 - hydroxy - 4 -  
methoxynaphthalene, 1 - hydroxy - 4 -  
ethoxynaphthalene, 1,4 - dihydroxy-  
naphthlene, 1,3 - dihydroxynaphtha-  
lene, 1 - hydroxy - 4 - aminonaphtha-  
lene, 1,5 - dihydroxynaphthalene, 1 -  
hydroxy - 2 - phenyl - 4 - methoxy-  
naphthalene, 1 - hydroxy - 2 - methyl -  
4 - methoxynaphthalene,  $\beta$  - naph-  
thol,  $\alpha$  - naphthol, 1,1' - dihydroxy -  
2,2' - binaphthyl, 4,4' - dimethoxy -  
1,1' - dihydroxy - 2,2' - binaphthyl,  
6,6' - dibromo - 2,2' - dihydroxy -  
1,1' - binaphthyl, 6,6' - dinitro - 2,2' -  
dihydroxy - 1,1' - binaphthyl and

	bis(2 - hydroxy - 1 - naphthyl)-methane;	mole of the organic silver salt (a). Colour toning agents may be used as an important additive in combination with these reducing agents. In particular, a colour toning agent is advantageously added when a black colour tone image is desired. The most general colour toning agents are phthalazinone and its derivatives. Other known effective colour toning agents are phthalimides, oxazinediones, pyrazoline - 5 - ones, oxazolinones and mercapto compounds, as described in Japanese Patent Application Nos. 41967/1972 and 50427/1873, Japanese Patent Disclosure No. 6077/1971, British Patent No. 1,379,868, and German OLS Nos. 2,140,406 and 2,141,063.	65
5	(4) Di- or polyhydroxybenzenes and hydroquinone monoethers: hydroquinone, methylhydroquinone, chlorohydroquinone, bromohydroquinone, phenylhydroquinone, hydroquinonemonosulphonate, <i>t</i> - octylhydroquinone, <i>t</i> - butylhydroquinone, 2,5 - dimethylhydroquinone, catechol, pyrogallol, resorcinol, 1 - chloro - 2,4 - dihydroxybenzene, 3,5 - di - <i>t</i> - butyl - 2,4 - dihydroxybenzoic acid, 2,4 - dihydroxybenzoic acid, 2,4 - dihydroxyphenyl sulphide, <i>p</i> - methoxyphenol, <i>p</i> - ethoxy - phenol, hydroquinone monobenzyl ether, 2 - <i>t</i> - butyl - 4 - methoxyphenol, 2,5 - di - <i>t</i> - butyl - 4 - methoxyphenol, hydroquinone mono - <i>n</i> - propyl ether, hydroquinone mono - <i>n</i> - hexyl ether, methyl gallate and propyl gallate.	Components (a), (b) and (c) are preferably dispersed in a binder (d) and applied into a support member as one layer containing all of the components (a), (b) and (c), or the components (a), (b) and (c) may be separately dissolved or dispersed in binders and applied as different layers.	70
10		The binder may be a material commonly used in this field. Ordinarily hydrophobic binders are desirable, but hydrophilic binders can be used. These binders may be transparent or semi-transparent natural materials such as gelatin and gelatin derivatives, mixtures of these materials with vinyl polymers of the latex type, cellulose derivatives and synthetic polymers. Suitable examples of these binders are gelatin, phthalated gelatin, polyvinyl butyral, polyacrylamide, cellulose acetate butyrate, cellulose, acetate propionate, polymethyl methacrylate, polyvinylpyrrolidone, polystyrene, ethyl cellulose, polyvinyl chloride, chlorinated rubbers, polyisobutylene, butadiene-styrene copolymers, vinyl chloride-vinyl acetate copolymers, vinyl acetate-vinyl chloride-maleic acid copolymers, polyvinyl alcohol, polyvinyl acetate, benzyl cellulose, cellulose diacetate, cellulose triacetate, cellulose propionate and cellulose acetate phthalate. These binders can be used individually or as a combination of two or more.	75
15	(5) Ascorbic acid or its derivatives and other photodecomposable reducing agents: <i>l</i> - ascorbic acid, isoascorbic acid, ascorbic acid mono-esters such as ascorbic acid monolaurate, monomyristate, monopalmitate, monostearate and monobehenate, ascorbic acid diesters such as ascorbic acid dilaurate, dimyristate, dipalmitate and distearate, furoin, benzoin, dihydroxyacetone, glyceric aldehyde and tetrahydroxyquinone rhodizonate.	90	
20		These binders are preferably used in an amount of 0.1 to 10 parts by weight, particularly 1/4 to 4 parts, per part of the organic silver salt (a). Where component (a) or (c) is a high molecular weight material also able to act as a binder, the use of such a separate binder can be omitted.	95
25	(6) 3 - Pyrazolidines and pyrazolones: 1 - phenyl - 3 - pyrazolidone, 4 - methyl - 4 - hydroxymethyl - 1 - phenyl - 3 - pyrazolidone and 1 - (2 - quinolyl) - 3 - methyl - 5 - pyrazolone.	The total quantity of silver applied to the support is generally from 0.2 to 3 g, preferably 0.3 to 2 g, per square metre of support. If too little is used, sufficient image density cannot be obtained, while if too much is used, the cost is increased without gaining additional photographic advantages.	100
30		If desired, matting agents such as starch, titanium dioxide, zinc oxide, silica and kaolin and/or fluorescent brightening agents such as the stilbenes, triazines, oxazoles and coumarins can be incorporated in the the.	110
35	(7) Reducing saccharides and others: glucose, lactose, <i>p</i> - hydroxyphenylglycine, hydroxytetroanic acid, N,N - di - (2 - ethoxyethyl)hydroxylamine, N,N - dialkyl - <i>p</i> - phenylenediamines, 5,7 - dihydroxy - 4 - methylcoumarin, kojic acid and $\beta$ - thujaplicin.	115	
40		120	
45		125	
50	These reducing agents can be used individually or as a combination of two or more. A suitable reducing agent is chosen to suit the organic silver salt (a) with which it is to be used. For example, silver behenate is rather difficult to reduce; therefore a rather strong reducing agent such as hydroquinone is suitable. On the other hand, silver caprate is relatively easy to reduce; therefore a relatively weak reducing agent such as bisphenol A is suitable.		
55			
60	The best amount of a given reducing agent (c) depends on the particular organic silver salt (a) and other additives such as any colour toning agent used but in general is from 0.1 to 5 moles, preferably 0.2 to 2 moles, per		

7 mally developable light-sensitive material according to the present invention.

5 The support can be coated using various coating methods, for example, an immersion method, an air-knife method, a curtain coating method and an extrusion coating method using a hopper as described in U.S. Patent No. 2,681,294. If required, two or more layers can be coated at the same time.

10 Some optical sensitizing dyes suitable for silver halide emulsions can be advantageously used to enhance the sensitivity of the light-sensitive material according to the invention. For example, a sensitizing dye can be added in the form of a solution or dispersion in an organic medium. Examples of suitable optical sensitizers are cyanines, merocyanines, rhodacyanines, styryl dyes and acidic dyes such as erythrosine, ecine and fluorescein. The amount of such a dye is generally 10<sup>-6</sup> to 10<sup>-3</sup> moles per mole of the organic silver salt (a). Suitable sensitizing dyes are described in U.S. Patents Nos. 3,152,904, 3,719,495 and 3,761,279, Belgian Patent No. 788,695, German OLS Nos. 2,328,868, 2,363,586, 2,405,713, 2,401,982 and 2,404,591, Japanese Patent Application No. 97050/1973, British Patent No. 1,417,382 and Japanese Patent Public Disclosure No. 4728/1971.

15 Furthermore, additives for preventing heat fog (an undesirable darkening when a non-exposed area is heated), for example mercury salts and U-halo compounds, can also be included in the light-sensitive material. These additives are described in U.S. Patent No. 3,589,903, German Patent Application OLS Nos. 2,326,865, 2,402,161 and 2,364,630 and Japanese Patent Application No. 43935/1973.

20 Acids, for example higher fatty acids and benzenesulphonic acid as described in Japanese Patent Application Nos. 37965/1973 and 106724/1973 and benzotriazole and its derivatives and 1-phenyl-5-mercaptopentetrazole can be added as a stabilizer.

25 If desired, an overcoated polymer layer can be provided on the light-sensitive layer in order to increase the transparency of the heat-developable light-sensitive layer, to increase the density of the image and to improve the shelflife. The thickness of such an overcoated layer is preferably from 1 to 20 microns. Examples of suitable polymers for the overcoated polymer layer are polyvinyl chloride, polyvinyl acetate, vinyl chloride-vinyl acetate copolymers, polyvinyl butyral, polystyrene, polymethyl methacrylate, polyurethane rubber, xylene resin, benzyl cellulose, ethyl cellulose, cellulose acetate butyrate, cellulose diacetate, cellulose triacetate, polyvinylidene chloride, chlorinated polypropylene, polyvinylpyrrolidone, cellulose propionate, polyvinyl formal, cellulose acetate phthalate, polycarbonate and cellulose acetate propionate.

30 When a material such as kaolin or silica

35 is contained in the overcoated layer, the material can be written on with a ball-point pen or pencil. An ultraviolet absorber such as a diaminostilbenesulphonic acid derivative, an imidazole derivative, a coumarin derivative or a higher fatty acid, e.g. an aliphatic carboxylic acid having at least 10 carbon atoms such as behenic acid, stearic acid, palmitic acid or lauric acid, can be incorporated in an overcoated layer. Furthermore, a phenolic coupler or colour-forming coupler having an active methylene group can be used in combination with a *p*-phenylenediamine as a reducing agent so as to form a colour image, as is described in U.S. Patent No. 3,531,286.

40 The light-sensitive material may be image-wise exposed, e.g. for 10<sup>-7</sup> sec. to 100 sec., preferably 10<sup>-6</sup> to 10 sec., to a light source such as a xenon lamp, a tungsten lamp, a mercury lamp or a fluorescent copying lamp and then developed simply by heating until a visible image is obtained. A suitable heating temperature is generally 80 to 180°C, preferably 110 to 150°C. Higher or lower temperatures imply shorter or longer heating durations respectively, a suitable duration being generally from 1 to 60 seconds.

45 The heating for development of the light-sensitive material can be performed for example by bringing the light-sensitive material into contact with a simple heated plate or platen or with a heated drum, by passing the material through a heated region or by using a high frequency heating or a laser beam.

50 The following examples describe the invention in greater detail and also describe comparative materials. All parts, percentages and ratios are by weight unless otherwise indicated.

55

60

65

70

75

80

85

90

95

100

105

110

115

120

125

EXAMPLE 1

3.4 Grams of behenic acid were dissolved in 100 ml of toluene at 60°C. The solution was mixed with stirring with 100 ml of aqueous nitric acid at 60°C (pH 2.0 at 25°C). To the resultant mixed solution kept at 60°C there were simultaneously added, with stirring, (i) an aqueous solution obtained by adding concentrated aqueous ammonia to 80 ml of an aqueous solution containing 1.7 g of silver nitrate, to form a silver ammonium complex salt, and then adding water to make the total volume 100 ml, and (ii) 50 ml of an aqueous solution of 0.047 g of ammonium bromide, 0.001 g of ammonium iodide and 0.0025 g of ammonium rhodium (III) hexachloride. Thus, silver behenate and silver iodobromide were simultaneously formed in the presence of the rhodium compound. The reaction product, allowed to stand at room temperature for 20 minutes, separated into an aqueous phase and a toluene phase. After the aqueous phase was removed, 400 ml of fresh water was added to the toluene phase

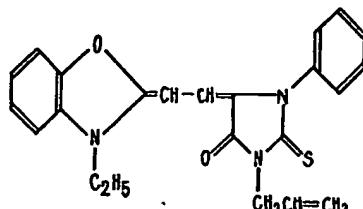
and the product was washed and the water decanted. Then 400 ml of methanol was added to the product, which was centrifuged, to yield a mixture comprising silver behenate, silver iodobromide and the rhodium compound. 4 Grams of spindle-shaped crystals having a length of about 0.9 microns and a width of about 0.03 micron were obtained.

2.5 Grams of the resulting mixture of silver behenate and silver iodobromide were added to 25 g of an isopropanol solution containing 2 g of polyvinyl butyral and the mixture was ball-milled for 1 hour to prepare a polymer dispersion of the silver salt.

To 25 g of the resulting polymer dispersion the following components were added to prepare a thermally developable light-sensitive coating composition and then the composition was applied to an art paper support at a rate of 0.5 g of silver per square metre of the support, this giving a thermally developable Light-Sensitive Material (A) according to the invention. For comparison, another Light-Sensitive Material (B) was similarly prepared using a mixture of silver behenate and silver iodobromide in an analogous manner to the above but without adding the rhodium compound.

30	mercuric acetate (heat fog inhibitor) (1% methanol solution)	1 ml
35	Dye (see below) (0.025% 2-methoxyethanol solution)	1 ml
	phthalazinone (colouring toning agent) (2.5% 2-methoxyethanol solution)	5 ml
40	2,2'-methylene-bis(6-t-butyl-4-methylphenol) reducing agent (25% 2-methoxyethanol solution)	3 ml
45	tetrabromophthalic acid (anhydrous) (0.5% methanol solution)	2 ml
	behenic acid (3% 2-methoxyethanol solution)	5 ml

The Dye above had the formula:



These two Light-Sensitive Materials (A) and (B) were exposed through an optical wedge, and heated and developed at 120°C for

20 seconds. In each Material, the difference between the logarithms of the exposure quantities giving rise to respective image densities of (fog + 0.6) and of (fog + 0.1) was determined and found to be 0.35 for Light Sensitive Material (A) and 0.95 for Light-Sensitive Material (B). As is evident from this result, Light-Sensitive Material (A) using a rhodium salt shows a high contrast. Where a negative image was produced from a positive original by reflection printing using Light-Sensitive Material (A) or (B) and a positive image was again reproduced from this negative image as an original by transmission printing, a high contrast, sharp positive image was obtained in the case of Light-Sensitive Material (A), while only a low contrast, obscure positive image was obtained in the case of Light-Sensitive Material (B).

#### Preparation 1

6 Grams of benzotriazole were dissolved at 50°C in 100 ml of isopentyl acetate and the solution was cooled to -15°C. To the solution was added, with agitation using a stirrer, a solution prepared by dissolving 8.5 g of silver nitrate in 100 ml of aqueous nitric acid (pH 2.0 at 25°C) and adjusting the temperature to 3°C, thus giving a dispersion containing fine crystals of silver benzotriazole. This dispersion, allowed to stand at room temperature (i.e. 20-30°C) for 20 minutes, separated into an aqueous phase and an isopentyl acetate phase. After the aqueous phase was removed, 400 ml of water were added to the isopentyl acetate phase, the product washed and the water decanted. Then 400 ml of methanol were added and the dispersion centrifuged to yield 8 g of silver benzotriazole having a particle size of a diameter of about 1 micron. 2.5 Grams of this silver benzotriazole were added to 40 ml of methyl ethyl ketone solution containing 4 g of ethyl cellulose and the mixture was ball milled for 1 hour to prepare a polymer dispersion of the silver benzotriazole.

#### EXAMPLE 2

To 45 g of silver benzotriazole dispersion from Preparation 1 were added the following components to prepare a thermally developable light-sensitive composition. The composition was applied to a paper support (which had been surface-coated with clay and styrene-butadiene rubber) at a rate of 1 g of silver per square metre of support, thus giving a thermally developable Light-Sensitive Material (A) according to the invention. For comparison, a thermally developable Light Sensitive Material (B) was prepared as above but without adding the rhodium compound.

55

60

65

70

75

80

85

90

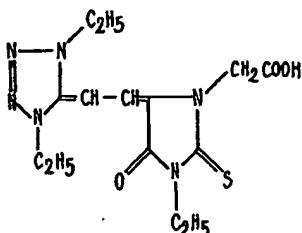
95

100

105

	methyl ethyl ketone	20	ml	g of N-bromosuccinimide (silver-halide-forming component), stirred for 90 minutes and allowed to stand. To the dispersion, now at 30°C, were added with stirring the following components in order every 5 minutes to prepare a thermally developable light-sensitive coating composition and the composition was coated on an art paper at a rate of 0.4 g of silver per square metre, thus giving a thermally developable Light-Sensitive Material (A) according to the invention.	55
5	cadmium iodide (silver - halide-forming component) (8.5% methanol solution)	1.5	ml		
10	ammonium rhodium (III) hexachloride (0.1% aqueous solution)	3	ml		
15	ascorbic acid monopalmitate ascorbic acid dipalmitate (reducing agent) (2 g of each in 10 ml of 2 - methoxy ethanol)	10	ml		
	N - ethyl - N' - dodecylurea (development accelerator) (2.5% 2 - methoxyethanol solution)	2	ml		
	Dye (see below) (0.015% 2 - methoxyethanol solution)	2	ml		

The Dye above had the formula



20 Both Light-Sensitive Materials (A) and (B) were treated in a similar manner to Example 1. Development was carried out by heating at 130°C for 10 seconds. The differences in log (exposure quantity), on the same bases as in Example 1, were: (A)—0.61; and (B)—1.04. As is evident from this result, Light-Sensitive Material (A) exhibits a higher contrast.

25

#### Preparation 2

30 1.9 Grams of sodium hydroxide were dissolved in 100 ml of water and mixed and emulsified at 25°C with a solution of 12 g of lauric acid in 100 ml of toluene. A solution of 8.5 g of silver nitrate in 50 ml of water was added thereto. An aqueous phase and a toluene phase containing silver laurate separated. After removing the aqueous phase, the toluene phase was dispersed with 200 ml of methanol and the dispersion centrifuged to yield 12 g of silver laurate spindle-shaped crystals having a length of about 3 microns.

35

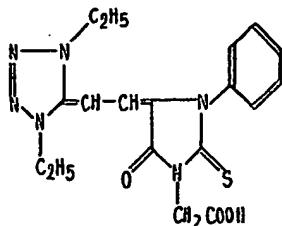
#### EXAMPLE 3

40 6 Grams of the silver laurate from Preparation 2 and 12 g of polyvinyl butyral were dispersed in 70 g of isopropyl alcohol using a mixer to prepare a polymer dispersion of the silver salt. This polymer dispersion of the silver salt was kept at 50°C, stirred with a stirrer, mixed with 0.003 g of ammonium rhodium (III) hexachloride, stirred for 20 minutes, allowed to stand, mixed with 0.15

45

	Dye (see below) (0.015% 2 - methoxyethanol solution)	10	ml	65
	phthalazinone (colour toning agent) (3% methanol solution)	50	ml	
	2,2 - bis(3,5 - dimethyl - 4 - hydroxyphenyl) - propane (20% acetone solution)	300	ml	70
	stearic acid (3% 2 - methoxyethanol solution)	15	ml	

The Dye above had the formula



75

For comparison, another heat-developable Light-Sensitive Material (B) was prepared in a similar manner but without adding the rhodium compound.

On both of Light-Sensitive Materials (A) and (B) was further coated a 10% acetone solution of cellulose diacetate containing 1.5% of silicon dioxide to form an overcoated layer.

Both materials were stepwise exposed through a wedge as in Example 1 and then heated and developed at 120°C for 10 seconds. The logarithmic differences on the bases explained in Example 1 were: (A)—0.45; (B)—1.02.

As is evident from this result, Light-Sensitive Material (A) exhibits a high contrast.

When a positive image was reproduced in the similar manner to Example 1, Light-Sensitive-Material (A) provided a much sharper positive image.

80

85

90

95

**COMPARISON EXAMPLE 1**  
8.6 Grams of capric acid were dissolved in 100 ml of butyl acetate kept at 5°C, stirred with a stirrer, mixed with 50 ml of a 0.4% aqueous solution of hydrobromic acid and emulsified. 50 ml of an aqueous

100

5 solution of silver nitrate ammonium complex salt containing 8.5 g of silver nitrate (cooled to 5°C) was added to the resulting emulsion over a 30-second period to react the capric acid and hydrogen bromide simultaneously with silver ion to form silver caprate and silver bromide. The aqueous phase was removed and the butyl acetate phase containing both silver salts was dispersed in 120 g of 15% isopropanol solution of polyvinyl butyral to prepare a polymer dispersion of the silver salt

10 To this polymer dispersion were added the following components to prepare a light-sensitive coating composition, which was applied to a coated paper at a rate of 1.0 g of silver per square metre of the support, thus making thermally developable Light-Sensitive Material (A), not according

20 to the invention.

25	mercuric acetate (heat fog inhibitor) (1% methanol solution)	10 ml
	rhodium bromide (4% methanol dispersion)	4 ml
30	tetrachlorotetrabromofluorescein (Dye) (0.025% methanol solution)	70 ml
	phthalazinone (colour toning agent) (2.5% 2 - methoxyethanol solution)	25 ml
	bisphenol A (reducing agent) (70% 2 - methoxyethanol solution)	70 ml

35 For comparison, another thermally developable Light-Sensitive Material (B) (also not according to the invention) was prepared in a similar manner but without adding the rhodium bromide. These Light-Sensitive materials were exposed through a wedge and developed by heating at 140°C for 5 seconds, in a similar manner to Example 2. The logarithmic differences, determined as explained in Example 1, were: (A)—1.20; (B) —1.08. As is evident from this result, Light-Sensitive Material (A) exhibits even a lower contrast than Material (B). That is, rhodium bromide is not effective.

#### EXAMPLE 4

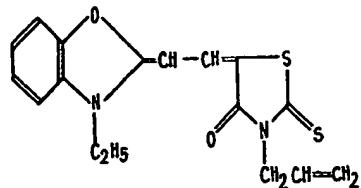
50 3.4 Grams of behenic acid were dissolved in 100 ml of benzene at 60°C. With stirring, 100 ml of aqueous nitric acid (pH 2.0 at 25°C) containing 7 mg of rhodium nitrate were added while keeping the resulting mixed solution at 60°C. With further stirring, a solution was added which had been obtained by adding aqueous ammonia to about 80 ml of an aqueous solution containing 1.7 g of silver nitrate to form a silver ammonium complex salt and then adding water to make up to 100 ml, thus yielding fine crystals of silver behenate containing a rhodium com-

5 pound. The resulting dispersion, allowed to stand at room temperature for 20 minutes, separated into an aqueous phase and a toluene phase. After removing the aqueous phase, 400 ml of fresh water was further added to the toluene phase, the product washed and the water decanted. Then 400 ml of methanol was added to the toluene phase and the mixture was centrifuged, thus giving 4 g of spindle-shaped silver behenate crystals containing the rhodium compound, the crystals having a length of about 1 micron and width of about 0.05 micron.

70 2.5 Grams of the resultant silver behenate was added to 20 ml of an isopropyl alcohol solution containing 2 g of polyvinyl butyral and the mixture was then ball-milled for 1 hour to prepare a polymer dispersion of the silver salt. To 20 ml of this polymer dispersion there were added the following component to prepare a light-sensitive composition, which was coated onto a photographic original paper at a rate of 0.6 g of silver per square metre of the support, thus giving a thermally developable Light-Sensitive Material (A) according to the invention.

85	ammonium bromide (silver - halide - forming component) (2.5% methanol solution)	1 ml	90
	Dye (see below) 0.025% 2 - methoxyethanol solution)	1 ml	
	2,2' - methylene - bis(6 - t - butyl - 4 - methylphenol) (reducing agent) (20% acetone solution)	3 ml	95
	phthalazinone (colour toning agent) (2.5% 2 - methoxyethanol solution)	3 ml	100
	anhydrous tetrabromophthalic acid (stabilizer) (0.6% methanol solution)	1 ml	

The Dye above had the formula:



105 For comparison, a thermally developable Light-Sensitive Material (B) was prepared in a similar manner but without adding the rhodium nitrate and a thermally developable Light-Sensitive Material (C) was prepared in a similar manner but using a equimolar amount of rhodium bromide (not according to the invention) in place of the rhodium nitrate and without using the ammonium bromide. The materials were exposed and developed by heating for 10 seconds at 120°C.

110

70

75

80

85

95

100

110

115

The logarithmic differences on the basis explained in Examples 1 were: (A)—0.54; (B)—0.96; and (C)—1.50. As is evident from this result, Light-Sensitive Material (A) using the rhodium salt exhibited a higher contrast and rhodium halides are not effective for the purpose of the invention.

## EXAMPLE 5

0.8 Grams of cetyl ethyldimethylammonium bromide and 0.05 g of potassium rhodium (II) hexachloride were dissolved in 100 ml of water to prepare a solution, which was mixed with 100 ml of toluene and emulsified. To this emulsion was added a solution of 0.425 g of silver nitrate in 10 ml of water to form silver bromide, in an emulsified state, containing a rhodium compound. A solution of 12 g of lauric acid in 100 ml of toluene and a solution of 1.9 g of sodium hydroxide in 100 ml of water were mixed, emulsified and added to the silver bromide 'emulsion'. Then a solution of 8.5 g of silver nitrate in 50 ml of water was added to form silver laurate. Thus, a mixture of silver bromide containing a rhodium compound in contact with silver laurate was obtained. This mixture was centrifuged and the precipitate dispersed, using a mixer, in 200 g of an ethanol solution containing 30 g of polyvinyl butyral to prepare a silver salt-polymer dispersion. To this silver salt-polymer dispersion were added the following components to prepare a light-sensitive composition, which was then applied to a photographic original paper at a rate of 0.5 g of silver per square metre of the support.

Dye see below (0.025% methanol solution)  
phthalazinone (colour toning agent) (3% methanol solution)  
2,2 - bis(3 - methyl - 4 - hydroxyphenyl) propane (reducing agent) (20% acetone solution)  
victoria blue B (whitening agent) (0.015% methanol solution)

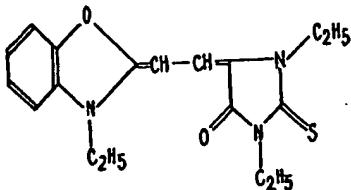
10 ml

35 ml

70 ml

2 ml

The Dye above had the formula:



Then the photographic paper was overcoated with a 10% tetrahydrofuran solution of a vinyl chloride-vinyl acetate copolymer con-

taining 1.5% of kaolin to a dry film thickness of 2 microns, to produce thermally developable Light-Sensitive Material (A), according to the invention.

55

For comparison, another Light-Sensitive Material (B) was prepared in a similar manner but without using the rhodium compound. The materials were exposed and developed by heating at 130°C for 30 seconds. The logarithmic differences on the basis explained in Example 1 were: (A)—0.48; and (B)—1.20. As is evident from this result, Light-Sensitive Material (A) containing the rhodium compound exhibited higher contrast.

60

65

## WHAT WE CLAIM IS:—

1. A thermally developable light-sensitive photographic material comprising a support having thereon in at least one layer

70

(a) an organic silver salt,  
(b) a catalytic amount of a light-sensitive silver halide, or a halogen compound capable of reacting with the organic silver salt (a) to form a catalytic amount of light-sensitive silver halide,

75

(c) a reducing agent capable of reducing said organic silver salt to silver in the presence of an imagewise exposed catalytic amount of light-sensitive silver halide, and

80

(d) a rhodium compound selected from rhodium nitrate and



wherein M represents a monovalent cation, X represents a halogen atom,  $h$  is from 2 to 5,  $k$  is 1 or 2,  $l$  is from 5 to 11,  $m$  is 0 or 2, and  $p$  is from 0 to 12, said rhodium compound being in contact with the components (a) and (b).

85

2. A light-sensitive material as claimed in Claim 1, wherein said organic silver salt (a) is a silver salt of an organic compound having an imino group, a mercapto group, a thio group, a hydroxyl group or a carboxyl group.

90

3. A light-sensitive material as claimed in Claim 2, wherein said organic silver salt (a) is a silver salt of a fatty acid.

95

4. A light-sensitive material as claimed in Claim 2, wherein said organic silver salt (a) is any of the compounds listed in List 1 hereinbefore.

100

5. A light-sensitive material as claimed in any one of the preceding Claims, wherein the total amount of silver compound(s) in the said material is from 0.2 g to 3 g (as silver) per square metre of the support.

105

6. A light-sensitive material as claimed in Claim 5, wherein the total amount of the silver compound(s) in the said material is from 0.3 to 2 g (as silver) per square metre of the support.

110

7. A light-sensitive material as claimed in

any one of the preceding Claims, wherein the amount of the component (b) is from 0.001 to 0.5 moles per mole of the organic silver salt (a). 65

8. A light-sensitive material as claimed in Claim 7, wherein the amount of the component (b) is from 0.01 to 0.2 moles per mole of the organic silver salt (a). 70

9. A light-sensitive material as claimed in any one of the preceding Claims, wherein said reducing agent (c) is a substituted phenol, a substituted or unsubstituted bisphenol, a substituted or unsubstituted naphthol, a substituted or unsubstituted bisnaphthol, a di- or polyhydroxynaphthalene, a di- or polyhydroxybenzene, a hydroquinone monooether, ascorbic acid or a derivative thereof a photo-decomposable reducing agent, a 3-pyrazolidone, a pyrazolone, a reducing saccharide, p-hydroxyphenylglycine, hydroxytetronic acid, N,N-di-(2-ethoxyethyl)hydroxylamine, an N,N-di-alkyl-p-phenylenediamine, 5,7-dihydroxy-4-methylcoumarin, kojic acid or 4-isopropyltropolone. 75

10. A light-sensitive material as claimed in Claim 9, wherein said reducing agent (c) is any of the compounds listed in List 3 hereinbefore. 80

11. A light-sensitive material as claimed in any one of the preceding Claims, wherein the amount of said reducing agent (c) is from 0.1 moles to 5 moles per mole of the organic silver salt (a). 85

12. A light-sensitive material as claimed in Claim 11, wherein the amount of said reducing agent (c) is from 0.2 moles to 2 moles per mole of the organic silver salt (a). 90

13. A light-sensitive material as claimed in any one of the preceding Claims, wherein said rhodium compound. 95

$M_b[Rh_4X_1(OH)_m] \cdot pH_2O$

is any of the compounds listed in List 2 hereinbefore. 100

14. A light-sensitive material as claimed in any one of the preceding Claims, wherein the molar proportion of the rhodium compound (d) to the silver halide is from 0.0001:1 to 0.5:1. 105

15. A light-sensitive material as claimed in Claim 14, wherein said molar proportion is from 0.001:1 to 0.1:1. 110

16. A method of making a thermally developable light-sensitive photographic material as claimed in any one of the preceding Claims, comprising mixing said rhodium compound (d) with a stoichiometric excess of said organic silver salt (a) and with a halogen compound (b) capable of reacting with the organic silver salt to form a catalytic amount of silver halide, and applying the mixture and said reducing agent (c) to a support in at least one layer. 115

17. A method as claimed in Claim 16, wherein said halogen compound (b) is the chloride, bromide or iodide of hydrogen, ammonium or a metal or is a halogen-containing metal complex, an N-halo compound containing a  $-\text{CONX}'-$  group wherein X represents chlorine, bromine or iodine, an onium halide, triiodomethane, tribromomethane, 2-bromo-2-methylpropane, tetrabromomethane, triphenylmethyl chloride, triphenylmethyl bromide, 2-bromobutanoic acid, 2-bromoethanol, or benzophenone di-chloride. 120

18. A method of making a thermally developable light-sensitive photographic material as claimed in any one of Claims 1 to 16, comprising simultaneously forming said organic silver salt (a) and said catalytic amount of silver halide (b) in the presence of said rhodium compound (d), and applying the reaction mixture and said reducing agent (c) to a support in at least one layer. 125

19. A method of making a thermally developable light-sensitive photographic material as claimed in any one of Claims 1 to 16, comprising mixing said catalytic amount of light-sensitive silver halide (b) with said organic silver salt (a), adding said rhodium compound (d) to the mixture, and applying the mixture and said reducing agent (c) to a support in at least one layer. 130

20. A method of making a thermally developable light-sensitive material, substantially as described herein with reference to the making of Light-Sensitive Material (A) in any one of Examples 1 to 5. 135

21. A thermally developable light-sensitive photographic material made by a method as claimed in any one of Claims 16 to 20. 140

22. A light-sensitive material as claimed in any one of Claims 1 to 15 or 21, wherein the layer or layers coated on the support contains a binder. 145

23. A light-sensitive material as claimed in Claim 22, wherein the binder is present in an amount of from 0.1 to 10 parts by weight per part of the organic silver salt (a). 150

24. A light-sensitive material as claimed in Claim 23, wherein the binder is present in an amount of from 1/4 to 4 parts by weight per part of the organic silver salt (a). 155

25. A light-sensitive material as claimed in any one of Claims 1 to 15 or 21 to 24, further comprising, coated over said layer or layers, a top-coat protective polymer layer. 160

26. A method of developing a photographic material as claimed in any of Claims 1 to 15 or 21 to 25, which material has been image-wise exposed, comprising heating the material for a period of time until a visible image is obtained. 165

27. A method as claimed in Claim 26, wherein the material is heated to a temperature of from 80°C to 180°C. 170

28. A method as claimed in Claim 27, wherein the material is heated to a temperature of from 110°C to 150°C.

5 29. A method as claimed in Claim 26, 27 or 28, wherein the duration of the heating is from 1 to 60 seconds.

30. A material bearing a visible image developed by a method as claimed in any of Claims 26 to 29.

GEE & CO.,  
Chartered Patent Agents,  
Chancery House,  
Chancery Lane,  
London, WC2A 1QU,  
and  
39, Epsom Road,  
Guildford, Surrey,  
Agents for the Applicants.

Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1977  
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from  
which copies may be obtained.